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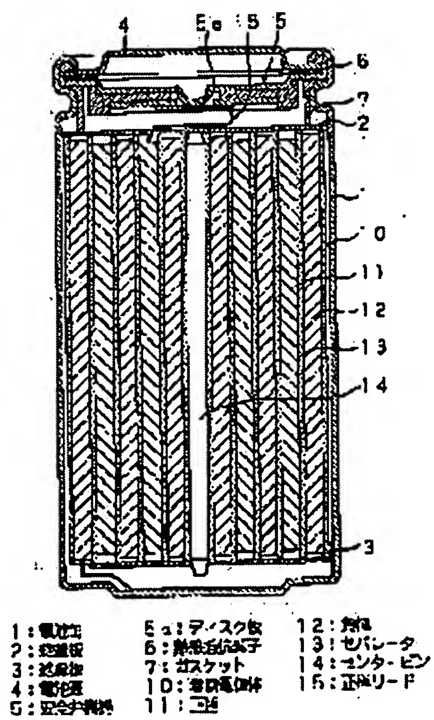
(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery superior in high temperature storage characteristics and load characteristics.

SOLUTION: In the nonaqueous electrolyte secondary battery equipped with a positive electrode having a positive electrode mixture layer composed of manganese containing oxide and nickel containing oxide as the main body, with a negative electrode comprised by containing at least one kind among lithium metal, lithium alloy or a material capable of doping/de-doping lithium, and with the nonaqueous electrolyte, Li2CO3 is contained in the positive electrode mixture layer, and the content of the Li2CO3 is in the range larger than 0 wt.% and not more than 5 wt.% in the positive electrode mixture layer.



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* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery equipped with the positive electrode containing the nickel content oxide containing the manganese content oxide, the lithium, and nickel (nickel) containing a lithium (Li) and manganese (Mn).
[0002]
[Description of the Prior Art] In recent years, with the advance of an electronic technique, many small portable electronic equipment, such as a camcorder/movie (video tape recorder), a cellular phone, or a laptop computer, spreads, and those miniaturizations and lightweight-izing are attained. Then, as a portable power source used for them, it is small and lightweight and development of the cell which has a high energy consistency, especially a rechargeable battery is furthered. The rechargeable lithium-ion battery which used nonaqueous electrolyte especially is greatly expected from high energy density being obtained compared with a lead cell or a nickel cadmium battery.
[0003] As a positive-electrode ingredient of this rechargeable lithium-ion battery, a lithium cobalt multiple oxide, a lithium manganese multiple oxide, lithium nickel complex oxide, etc. are put in practical use. Among these, the lithium cobalt multiple oxide is most excellent in the balance in each side, such as cell capacity, cost, and thermal stability, and is used widely now. On the other hand, although a lithium manganese multiple oxide has a fault, like cell capacity is low and some is bad as for an elevated-temperature preservation property and there is a fault, like thermal stability of lithium nickel complex oxide is low a little, these are excellent in the price of a raw material, and the field of adequate supply, and research is advanced towards the future activity. For example, while complementing both fault with recently by mixing and using a lithium manganese multiple oxide and lithium nickel complex oxide, the expansion and contraction of a positive electrode in charge and discharge are controlled, and the technique of raising a charge-and-discharge cycle property is proposed (refer to JP,8-45498,A).
[0004]
[Problem(s) to be Solved by the Invention] However, in the rechargeable battery currently indicated by JP,8-45498,A, when saved, for example under 45 degrees C - 60 degrees C hot environments, there was a problem that a property will fall. Although the capacity in a heavy load (condition that current density is large), and a high termination electrical potential difference was calculated when especially used for information terminals, such as a cellular phone, sufficient value was not able to be acquired after elevated-temperature preservation. Moreover, in the above-mentioned secondary ****, there was a problem that a charge-and-discharge cycle property could not fully be raised depending on the particle size of a lithium manganese multiple oxide and lithium nickel complex oxide.
[0005] Therefore, this invention is proposed for the purpose of offering the rechargeable battery which was excellent in the elevated-temperature preservation property, and was further excellent also in the load characteristic.
[0006]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention A

lithium (Li) and manganese (Mn), At least one sort of 1st elements chosen from the group which consists of the metallic elements and boron (B) other than manganese, The manganese content oxide whose mole ratio [as opposed to the above-mentioned manganese including oxygen (O)] (the 1st element/manganese) of the 1st element of the above is within the limits of 0.5/1.5 or less [0.01/1.99 or more], At least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, and nickel (nickel) and nickel, The positive electrode equipped with the positive-electrode binder layer which makes a subject the nickel content oxide whose mole ratio (the 2nd element/nickel) of the 2nd element of the above to the above-mentioned nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] including oxygen, In a nonaqueous electrolyte rechargeable battery equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium, and nonaqueous electrolyte Li2CO3 contains in the above-mentioned positive-electrode binder layer, and the content of this Li2CO3 is larger than 0 % of the weight in the above-mentioned positive-electrode binder layer, and is characterized by being 5 or less % of the weight of the range.
[0007] Since Li2CO3 contains the nonaqueous electrolyte rechargeable battery concerning this invention constituted as mentioned above in the positive-electrode binder layer with the content of the above-mentioned range, it is excellent in an elevated-temperature preservation property, and excellent in a load characteristic.
[0008]
[Embodiment of the Invention] Hereafter, the concrete example of this invention is explained in full detail with reference to a drawing.
[0009] The cross-section configuration of the nonaqueous electrolyte rechargeable battery concerning the gestalt of the 1 operation of this invention to drawing 1 is shown. This nonaqueous electrolyte rechargeable battery is called cylindrical [so-called], and has mostly the rolled electrode object 10 with which a band-like positive electrode 11 and a band-like negative electrode 12 were wound around the interior of the hollow cylinder-like cell can 1 through the separator 13. The cell can 1 is constituted by the iron (Fe) with which plating of nickel was carried out, the end section is closed, and the other end is opened wide. Inside the cell can 1, the electric insulating plates 2 and 3 of a pair are perpendicularly arranged to the winding peripheral surface, respectively so that the rolled electrode object 10 may be inserted.
[0010] the relief valve device 5 prepared in the open end section of the cell can 1 inside the cell lid 4 and this cell lid 4, and the feeling-of-heat resistance element (Positive Temperature Coefficient-TC component) 6 -- a gasket 7 -- minding -- by being closed, it is attached and the interior of the cell can 1 is sealed. The cell lid 4 is constituted by the same ingredient as the cell can 1. It connects with the cell lid 4 electrically through the feeling-of-heat resistance element 6, and disk plate 5a is reversed and the relief valve device 5 disconnects the electrical installation of the cell lid 4 and the rolled electrode object 10, when the internal pressure of a cell becomes more than fixed with an internal short circuit or heating from the outside. The feeling-of-heat resistance element 6 restricts a current according to increase of resistance, if temperature rises, it prevents unusual generation of heat by the high current, and is constituted by barium titanate system semiconductive ceramics. The gasket 7 is constituted by the insulating material and asphalt is applied to the front face.
[0011] The rolled electrode object 10 is wound focusing on the center pin 14. The positive-electrode lead 15 which consists of aluminum (aluminum) etc. is connected to the positive electrode 11 of the rolled electrode object 10, and the negative-electrode lead 16 which consists of nickel etc. is connected to the negative electrode 12. By welding the positive-electrode lead 15 to the relief valve device 5, it connects with the cell lid 4 electrically, and the negative-electrode lead 16 is welded to the cell can 1, and is connected electrically.
[0012] The positive electrode 11 is constituted by for example, the positive-electrode binder layer and the positive-electrode current collection body whorl, and has the structure where the positive-electrode binder layer was prepared in both sides or one side of a positive-electrode current collection body whorl. The positive-electrode current collection body whorl is constituted by metallic foils, such as aluminium

foil, a nickel foil, or a stainless steel foil.
[0013] In the positive-electrode binder layer, the manganese content oxide and nickel content oxide which are described below contain as positive active material, and binders, such as electric conduction material, such as a graphite, and polyvinylidene fluoride, contain further if needed.
[0014] And Li_2CO_3 contains in this positive-electrode binder layer. And the content of this Li_2CO_3 is larger than 0 % of the weight in the above-mentioned positive-electrode binder layer, and let it be 5 or less % of the weight of the range.
[0015] When Li_2CO_3 does not contain in a positive-electrode binder layer, an elevated-temperature preservation property is not improved. On the other hand, since there are many rates that Li_2CO_3 which does not contribute to electronic conduction occupies when the content of Li_2CO_3 in a positive-electrode binder layer exceeds 5 % of the weight, the conductivity of a positive electrode falls and a load characteristic falls.
[0016] Therefore, with a nonaqueous electrolyte rechargeable battery, it excels in an elevated-temperature preservation property by Li_2CO_3 containing in a positive-electrode binder layer by the content of this Li_2CO_3 being larger than 0 % of the weight to a positive-electrode binder layer, and being 5 or less % of the weight of the range, and excels in a load characteristic.
[0017] Manganese content oxide contains at least one sort of 1st elements chosen from the group which consists of the metallic elements and boron other than a lithium, manganese, and manganese, and oxygen. This manganese content oxide has for example, cubic (spinel) structure or tetragonal structure, and the 1st element is permuted by the manganese atom and exists in the site of a manganese atom part. When the chemical formula of a manganese content oxide expresses the 1st element with Ma, it is shown by $Li_xMn_{2-y}Ma_yO_4$. Here, the value of x is within the limits of $0.9<=x<=2$, and the value of y is within the limits of $0.01<=y<=0.5$. That is, presentation ratio Ma/Mn of the 1st element to manganese is or more 0.01/1.99 0.5/1.5 or less range in a mole ratio.
[0018] As the 1st element of the above, specifically Iron (Fe), cobalt (Co), Nickel (nickel), copper (Cu), zinc (Zn), aluminum (aluminum), Tin (Sn), chromium (Cr), vanadium (V), titanium (Ti), At least one sort chosen from the group which consists of magnesium (Mg), calcium (calcium), strontium (Sr), boron (B), a gallium (Ga), an indium (In), silicon (Si), and germanium (germanium) is desirable. The manganese content oxide which makes these the 1st element can be obtained comparatively easily, and is chemically stable.
[0019] Nickel content oxide contains at least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, nickel, and nickel, and oxygen. This nickel content oxide has the layer structure, and in a part of site of a nickel atom, the 2nd element is permuted by the nickel atom and exists. When the chemical formula of a nickel content oxide expresses the 2nd element with Mb, it is typically shown by $LiNi_{1-z}Mb_zO_2$. In addition, the presentation ratio of a lithium and oxygen may not be Li:O=1:2 and the value of z is within the limits of $0.01<=z<=0.5$. That is, presentation ratio Mb/nickel of the 2nd element to nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] in a mole ratio.
[0020] At least one sort chosen from the group which consists of iron, cobalt, manganese, copper, zinc, aluminum, tin, chromium, vanadium, titanium, magnesium, calcium, strontium, boron, a gallium, an indium, silicon, and germanium as the 2nd element of the above is desirable. It is because the nickel content oxide which makes these the 2nd element can be obtained comparatively easily and is chemically stable.
[0021] By permuting by other elements which mentioned above some of manganese or nickel, these manganese content oxide and a nickel content oxide can be considered that the crystal structure is stable, and, thereby, can raise an elevated-temperature preservation property now with this nonaqueous electrolyte rechargeable battery. It is because the heavy load discharge capacity after elevated-temperature preservation will fall if sufficient effectiveness cannot be acquired if making presentation ratio Ma/Mn of the 1st element to manganese or less [0.01/1.99 or more] into 0.5/1.5 by the mole ratio, and making presentation ratio Mb/nickel of the 2nd element to nickel or less [0.01/0.99 or more] into 0.5/0.5 by the mole ratio has few amounts of permutations than this, but there are more amounts of

permutations than this.
[0022] The mixing ratio of the manganese content oxide and nickel content oxide in a positive electrode 11 is a mass ratio, and it is desirable that they are the nickel content oxides 90-20 to the manganese content oxides 10-80. It is because a manganese content oxide deteriorates remarkably in the electrolyte later mentioned in an elevated-temperature ambient atmosphere, so internal resistance will increase after elevated-temperature preservation and capacity will fall, if there are more contents of a manganese content oxide than this. Moreover, a nickel content oxide is because discharge potential is low, so the heavy load discharge capacity in the high potential cut-off after elevated-temperature preservation will become low if there are more contents of a nickel content oxide than this.
[0023] As for the mean particle diameter of a manganese content oxide and a nickel content oxide, it is desirable that it is 30 micrometers or less, respectively. It is because the expansion and contraction of a positive electrode 11 accompanying charge and discharge cannot fully be controlled and sufficient charge-and-discharge cycle property cannot be acquired in ordinary temperature, if mean particle diameter is larger than this.
[0024] In addition, these manganese content oxide and nickel content oxide can be obtained by carrying out heating baking at the temperature of 600 degrees C - 1000 degrees C into an oxygen existence ambient atmosphere, after preparing the compound containing the compound containing a lithium compound, a manganese compound, and the 1st element or a lithium compound, a nickel compound, and the 2nd element, respectively and mixing by the ratio of a request of them. As a compound of a raw material, a carbonate, a hydroxide, an oxide, a nitrate, or an organic-acid salt is used, respectively in that case.
[0025] The negative electrode 12 has the structure where the negative-electrode binder layer was prepared in both sides or one side of a negative-electrode current collection body whorl, respectively, like the positive electrode 11. The negative-electrode current collection body whorl is constituted by metallic foils, such as copper foil, a nickel foil, or a stainless steel foil. The negative-electrode binder layer consists of potentials not more than 2V possible [occlusion and breaking away] including any one sort of the negative-electrode ingredient in which a dope and a dedope are possible, or two sorts or more in the lithium on the basis of for example, a lithium metal or lithium metal potential, for example, contains binders, such as polyvinylidene fluoride, further if needed.
[0026] A lithium metal and a lithium alloy compound are mentioned as a negative-electrode ingredient in which a dope and a dedope of a lithium are possible. A lithium alloy compound here is expressed for example, with the chemical formula $D_sE_tLi_u$. In this chemical formula, D expresses at least one sort in the metallic element which can form a lithium, an alloy, or a compound, and a semi-conductor element, and E expresses at least one sort in metallic elements other than a lithium and D, and a semi-conductor element. Moreover, the values of s, t, and u are $s> 0$, $t>=0$, and $u>=0$, respectively.
[0027] Here, as the metallic element which can form a lithium, an alloy, or a compound, or a semi-conductor element, desirable especially preferably, 4B group's metallic element or semi-conductor element is silicon or tin, and is silicon most preferably. As the metal which can form a lithium, an alloy, or a compound, or a semi-conductor, each metals of Mg, B, aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, Bi, Cd, Ag, Zn, Hf, Zr, and Y, those alloy compounds, for example, Li-aluminum, Li-aluminum-M (M consists or more of one ofA [2],B [3], and 4B transition-metals elements among formula.) AlSb, CuMgSb, etc. can be mentioned. Moreover, these alloys or compounds are also desirable, for example, M_xSi (M is one or more metallic elements except Si among a formula, and x is $0< x$.) and M_xSn (M is one or more metallic elements except Sn among a formula, and x is $0< x$.) are mentioned. Specifically, SiB_4, SiB_6, Mg_2Si, Mg_2Sn, nickel2Si, $TiSi_2$, $MoSi_2$, $CoSi_2$, $NiSi_2$, $CaSi_2$ and $CrSi_2$, Cu_5Si, $FeSi_2$, $MnSi_2$, $NbSi_2$, $TaSi_2$, VSi_2 and WSi_2, or $ZnSi_2$ is mentioned.
[0028] Furthermore, as a negative-electrode ingredient, the lithium, the alloying or the element that can be compound-ized shown above, or a compound can also be used. That is, in this ingredient, one or more kinds of 4B group elements may be contained, and metallic elements other than 4B group containing a lithium may be contained. As such an ingredient, SiC, Si_3N_4, Si_2N_2O, germanium2N2O, SiO_x (x are $0< x<=2$ among a formula.), SnO_x (x are $0< x<=2$ among a formula.), LiSiO, LiSnO, etc.

can be illustrated.
[0029] As a negative-electrode ingredient in which a dope and a dedope of a lithium are possible, a carbon material, a metallic oxide, or polymeric materials is mentioned. As a carbon material, nongraphitizing carbon, an artificial graphite, corks, graphite, glassy carbon, an organic high molecular compound baking object, a carbon fiber, activated carbon, or carbon black is mentioned, for example. Among these, corks have pitch coke, needle coke, or petroleum coke, and an organic high-molecular-compound baking object says what calcinated and carbonized polymeric materials, such as phenol resin and furan resin, at suitable temperature to it. Moreover, as a metallic oxide, ferrous oxide, ruthenium oxide, molybdenum oxide, or the tin oxide is mentioned, and polyacethylene or polypyrrole is mentioned as polymeric materials.
[0030] The separator 13 is constituted by the porous membrane which consists of inorganic materials, such as a nonwoven fabric of the porous membrane which consists of an ingredient of polyolefine systems, such as polypropylene or polyethylene, or ceramics nature, and may be made into the structure which carried out the laminating of these two or more sorts of porous membrane.
[0031] The nonaqueous electrolyte which is liquefied nonaqueous electrolyte sinks into this separator 13. As for this nonaqueous electrolyte, lithium salt is dissolved in a non-aqueous solvent as an electrolyte salt. As a non-aqueous solvent, for example Propylene carbonate, ethylene carbonate, Diethyl carbonate, dimethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyl lactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, 4-MECHIRU 1, 3-dioxolane, It is desirable, and diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propionitrile, an anisole, acetic ester, butylate, or propionic-acid ester mixes 1 of any sorts of these, and two sorts or more, and is used.
[0032] As lithium salt, there are $LiClO_4$, $LiAsF_6$, $LiPF_6$, $LiBF_4$, LiB (C_6H_5), $LiCH_3SO_3$, $LiCF_3SO_3$, LiCl, LiBr, etc., for example, and 1 of any sorts of these and two sorts or more are mixed, and are used.
[0033] The nonaqueous electrolyte rechargeable battery constituted as mentioned above is equipped with the positive-electrode binder layer which Li_2CO_3 contains, and it is larger than 0 % of the weight, and since content of Li_2CO_3 in a positive-electrode binder layer is made into 5 or less % of the weight of the range, it is excellent in an elevated-temperature preservation property and a load characteristic.
[0034] This nonaqueous electrolyte rechargeable battery can be manufactured as follows, for example.
[0035] first -- as positive active material -- a manganese content oxide and a nickel content oxide, and the need -- responding -- an electric conduction agent and a binder -- mixing -- a positive electrode -- a mixture is prepared. subsequently, this positive electrode -- a mixture -- solvents, such as a N-methyl-2-pyrrolidone, -- distributing -- a paste-like positive electrode -- a mixture -- it considers as a slurry. this positive electrode -- a mixture -- after applying a slurry to a positive-electrode current collection body whorl and drying a solvent, compression molding is carried out with a roller press machine etc., a positive-electrode binder layer is formed, and a positive electrode 11 is produced.
[0036] In this positive-electrode binder layer, Li_2CO_3 is larger than 0 % of the weight, and contains in 5 or less % of the weight of the range. the content of Li_2CO_3 in a positive-electrode binder layer -- a positive electrode -- it considers as the above-mentioned range by adjusting the addition of Li_2CO_3 suitably at the time of Shirabe of a mixture.
[0037] By the way, Li_2CO_3 may be used as one sort of the synthetic powder of a manganese content oxide. When using Li_2CO_3 as one sort of the synthetic powder of a manganese content oxide, Li_2CO_3 may remain in a manganese content oxide after composition. Thus, it is larger than 0 % of the weight in the content of Li2CO [in / using the positive active material with which Li_2CO_3 remains / a positive-electrode binder layer]3, and good also as 5 or less % of the weight.
[0038] In addition, what is necessary is to mix with what has the few amount of survival of Li_2CO_3 which remained in positive active material suitably, and just to let content of Li_2CO_3 finally contained in a positive-electrode binder layer be the above-mentioned range, when there are many amounts of survival of Li_2CO_3 which remained in positive active material after composition of a manganese content oxide since it was unreacted.
[0039] subsequently, a negative-electrode active material and the need -- responding -- a binder -- mixing -- a negative electrode -- a mixture -- preparing -- this negative electrode -- a mixture -- solvents,

such as a N-methyl-2-pyrrolidone, -- distributing -- a paste-like negative electrode -- a mixture -- it considers as a slurry. this negative electrode -- a mixture -- after applying a slurry to a negative-electrode current collection body whorl and drying a solvent, compression molding is carried out with a roller press machine etc., a negative-electrode binder layer is formed, and a negative electrode 12 is produced.
[0040] Then, while attaching the positive-electrode lead 15 in a positive-electrode current collection body whorl by welding etc., the negative-electrode lead 16 is attached in a negative-electrode current collection body whorl by welding etc. Then, on both sides of the positive electrode 11 and negative electrode 12 which welded the point of the negative-electrode lead 16 to the cell can 1, and wound the positive electrode 11 and the negative electrode 12 while welding the point of winding and the positive-electrode lead 15 to the relief valve device 5 through the separator 13, it contains inside the cell can 1 with the electric insulating plates 2 and 3 of a pair. After containing a positive electrode 11 and a negative electrode 12 inside the cell can 1, nonaqueous electrolyte is poured into the interior of the cell can 1, and a separator 13 is infiltrated.
[0041] then, the open end of the cell can 1 -- the cell lid 4, the relief valve device 5, and the feeling-of-heat resistance element 6 -- a gasket 7 -- minding -- it fixes by closing. Thereby, the nonaqueous electrolyte rechargeable battery shown in drawing 1 is formed.
[0042] In addition, this invention can be suitably changed in the range which is not limited to an above-mentioned publication and does not deviate from the summary of this invention.
[0043] Therefore, in the above, although an example was given concretely and explained about the cylindrical nonaqueous electrolyte rechargeable battery which has winding structure, this invention is applicable also about the cylindrical nonaqueous electrolyte rechargeable battery which has other configurations. Moreover, it is applicable similarly about the nonaqueous electrolyte rechargeable battery which has various configurations, such as a mold with which it is not limited to a cylindrical shape about the configuration of a cell, and the electrode component was enclosed with the interior of coin molds other than cylindrical, a carbon button mold, a square shape, or a laminate film.
[0044] Moreover, although the case where the nonaqueous electrolyte which comes to dissolve an electrolyte salt in a non-aqueous solvent as nonaqueous electrolyte was used in the above was mentioned as the example and explained The gel electrolyte which this invention is not limited to this and consists of an electrolyte salt, a swelling solvent, and a matrix macromolecule as nonaqueous electrolyte, It can apply, also when the nonaqueous electrolyte ingredient which comes to mix the inorganic solid electrolyte which uses as a principal component the solid polymer electrolyte which makes-izing [an ion conductivity macromolecule and an electrolyte salt] come [compound], the ion conductivity inorganic ceramics, glass, an ionicity crystal, etc., and nonaqueous electrolyte is used.
[0045] For example, when using a gel electrolyte as nonaqueous electrolyte, as long as the ionic conductivity of a gel electrolyte is 1 or more mS/cm, the structure of the matrix macromolecule which constitutes the presentation of a gel electrolyte and a gel electrolyte may be what kind of thing.
[0046] As a concrete matrix giant molecule, it is possible to use the copolymer of a polyacrylonitrile, polyvinylidene fluoride, polyvinylidene fluoride, and poly hexafluoropropylene, polytetrafluoroethylene, poly hexafluoropropylene, polyethylene oxide, polypropylene oxide, poly FOSUFAZEN, a polysiloxane, polyvinyl acetate, polyvinyl alcohol, a polymethyl methacrylate, polyacrylic acid, polymethacrylic acid, a styrene butadiene rubber, nitril-butadiene rubber, polystyrene, a polycarbonate, etc. When electrochemical stability is especially taken into consideration, it is desirable to use a polyacrylonitrile, polyvinylidene fluoride, poly hexafluoropropylene, polyethylene oxide, etc.
[0047] Moreover, although it is difficult to specify generally from changing with compatibility of a matrix macromolecule and nonaqueous electrolyte, as for the weight of a matrix macromolecule required in order to produce a gel electrolyte, it is desirable to consider as 5 % of the weight - 50 % of the weight to nonaqueous electrolyte.
[0048]
[Example] Hereafter, this invention is explained based on a concrete experimental result.
[0049] an example 1 [production of a positive electrode] -- the manganese content oxide which mixes a lithium carbonate (Li_2CO_3), a manganese dioxide (MnO_2), and 3 oxidation Nichrome (CrO_3),

calcinates at the temperature of 850 degrees C for 5 hours, and contains chromium as a lithium, manganese, and the 1st element (Ma) in air first was produced.
[0050] Moreover, a lithium hydroxide (LiOH), 1 nickel oxide (NiO), and 1 cobalt oxide (CoO) were mixed, and the nickel content oxide which calcinates at the temperature of 750 degrees C for 5 hours, and contains cobalt as a lithium, nickel, and the 2nd element (Mb) in air was produced.
[0051] Subsequently, positive active material was obtained by mixing them as 50:50 by the weight ratio, after grinding the manganese content oxide and nickel content oxide which were obtained, respectively.
[0052] Moreover, the content of Li2CO3 contained in positive active material was 0.01 % of the weight. In addition, as measurement of the content of Li2CO3 contained in positive active material was shown below, it was performed.
[0053] First, the sulfuric acid decomposed the positive-active-material sample, and CO2 was made to generate. Subsequently, the solution of barium chloride and a sodium hydroxide was made to absorb this CO2. Subsequently, this solution was titrated with the acid standard solution, and the quantum of CO2 was carried out. And it converted from this CO2 amount and asked for the content of Li2CO2 contained in positive active material.
[0054] subsequently, this positive-active-material 91 weight section -- receiving -- as an electric conduction agent -- as the GURAFAITO 6 weight section and a binder -- the Pori fluoride PINIRIDEN 3 weight section -- mixing -- a positive electrode -- the mixture was prepared. and this positive electrode -- the mixture was dried and the positive electrode of a pellet type was obtained by the thing whose diameter is 15.5mm and which is fabricated disc-like.
[0055] [Production of a negative electrode] After applying the coal tar system pitch as a binder to the coal system corks 100 weight section as a filler for 30 weight sections and mixing at about 100 degrees C first, compression molding was carried out with the press machine, and the carbon molding object was produced by heat-treating at the temperature of 1000 degrees C or less. Then, after repeating pitch sinking in / heat treatment process which sinks in and heat-treats the coal tar system pitch which carried out melting to this carbon molding object below 200 degrees C below 1000 degrees C several times, in **************, it heat-treated at 2700 degrees C, and the graphitization molding object was produced. Then, grinding classification of this graphitization molding object was carried out, and it was presupposed that it is powdered.
[0056] When structural analysis was performed with the X-ray diffraction method about the obtained graphitization powder, the spacing of a field (002) was 0.337nm and C shaft microcrystal thickness of a field (002) was 50.0nm. Moreover, the true density for which it asked by the pycnometer was 2.23 g/cm3, bulk density was 0.83 g/cm3, and the average shape parameter was 10. furthermore, BET (Brunauer, Emmett, Teller) -- the specific surface area for which it asked by law was 4.4m2/g, and, for 31.2 micrometers and 10% particle size of accumulation, 12.3 micrometers and 50% particle size of accumulation were [mean particle diameter / 29.5 micrometers and a total of 90% particle size of the particle size distribution searched for with the laser diffraction method] 53.7 micrometers. In addition, the disruptive strength of the graphitization particle for which it asked using the Shimazu very small compression tester (Shimadzu make) was 7.0x107Pa by the average.
[0057] subsequently, the above-mentioned graphitization powder 35 weight section and the Mg2Si powder 55 weight section which are a negative-electrode active material -- as a binder -- the polyvinylidene fluoride 10 weight section -- mixing -- a negative electrode -- N-methyl pyrrolidone which a mixture is prepared and is a solvent -- distributing -- a negative electrode -- a mixture -- it considered as the slurry. and this negative electrode -- a mixture -- apply a slurry to homogeneity and both sides of the negative-electrode current collection body whorl which consists of band-like copper foil with a thickness of 10 micrometers were made to dry it, compression molding was carried out with the roll press machine, the negative-electrode binder layer was formed, and the negative electrode was produced by piercing to discoid with a diameter of 16mm.
[0058] [Preparation of nonaqueous electrolyte] The nonaqueous electrolyte which makes it come as an electrolyte salt into the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity % to dissolve LiPF6 at a rate of 1.0 mols/l. was prepared.

[0059] Using the positive electrode, the negative electrode, and nonaqueous electrolyte which were produced as mentioned above, below, as the nonaqueous electrolyte rechargeable battery of a coin mold was shown below, it was produced.
[0060] First, after containing the negative electrode with the negative-electrode can which consists of stainless steel and pouring nonaqueous electrolyte into a negative-electrode can, the separator which is the thickness of 50 micrometers in the product made from fine porosity polypropylene was allotted on the negative electrode. Subsequently, after arranging the positive electrode and pouring in nonaqueous electrolyte on a separator, the nonaqueous electrolyte rechargeable battery of a coin mold with an outer diameter [of 20mm] and a height of 1.6mm was obtained for the positive-electrode can equipped with the three-tiered structure which consists of aluminum, stainless steel, and nickel a negative-electrode can and by fixing in total through the obturation gasket made from polypropylene.
[0061] The content of Li2CO3 in examples 2 and 3 and the example 1 of a comparison - 3 positive-electrode binder layer produced the nonaqueous electrolyte rechargeable battery like the example 1 except being as in Table 1 shown below. In addition, the content of Li2CO3 was controlled by carrying out adding after mixing of Li2CO3.
[0062] After performing constant current constant-potential charge until cell voltage amounted to 4.2V in 1mA constant current first to the nonaqueous electrolyte rechargeable battery of the examples 1-3 produced as mentioned above and the examples 1-3 of a comparison, the charge-and-discharge cycle which carries out constant-current discharge to termination electrical-potential-difference (cut-off voltage) 2.5V by 1mA constant current was performed, and initial discharge capacity was measured.
[0063] Subsequently, in order to evaluate an elevated-temperature preservation property and a load characteristic, the charge and discharge test shown below was performed.
[0064] The charge-and-discharge cycle mentioned above was again performed after measurement of an initial <evaluation of elevated-temperature preservation property> above-mentioned discharge capacity. Subsequently, it saved for two weeks in 60-degree-C oven. Subsequently, once discharging to termination electrical-potential-difference 2.5V under 23-degree-C environment, discharge capacity was measured for the charge-and-discharge cycle as it is **** 10 cycles. And the peak price was made into recovery capacity among the acquired discharge capacity value, and it asked for the ratio of recovery capacity to initial discharge capacity by the percentage, and considered as the recovery capacity maintenance factor.
[0065] After charging until cell voltage amounted to 4.2V in <evaluation of load characteristic> 1mA constant current, the discharge capacity in 0.1C was measured and the discharge capacity in 3C was measured further. And it asked for the capacity factor (%) of 3C discharge capacity to 0.1C discharge capacity, and this capacity factor estimated the load characteristic.
[0066] The above measurement result is shown in Table 1 in accordance with the content of Li2CO3 in a positive-electrode binder layer.
[0067]
[Table 1]

	Li_2CO_3 (重量%)	初期 放電容量 (mAh)	高温保存特性 回復容量維持率(%)	高温保存特性 回復容量 (mAh)	負荷特性 容量比 (%)
実施例1	0.01	8.53	86.1	7.26	8.01
実施例2	2.0	8.37	88.7	7.42	78.2
実施例3	5.0	8.11	89.1	7.23	76.4
比較例1	0	8.54	76.3	6.51	80.2
比較例2	5.5	8.07	89.2	7.20	73.1
比較例3	10.0	7.69	89.4	6.87	31.4

Table 1 shows that the nonaqueous electrolyte rechargeable battery of an example 1 - an example 3 is excellent in an elevated-temperature preservation property and a load characteristic. Moreover, it turns out that an elevated-temperature preservation property improves, so that the content of Li2CO3 in a positive-electrode binder layer is made to increase.

[0068] However, since Li_2CO_3 which does not contribute to electronic conduction contains superfluously in a positive-electrode binder layer in the case of the nonaqueous electrolyte rechargeable battery of the example 2 of a comparison for which the content of Li_2CO_3 exceeds 5 % of the weight, and the example 3 of a comparison, it turns out that the conductivity of a positive electrode falls and a load characteristic falls.
[0069] Moreover, since the nonaqueous electrolyte rechargeable battery of the example 1 of a comparison whose content of Li_2CO_3 is 0 % of the weight has the bad elevated-temperature preservation property, it turns out that it is not desirable practically.
[0070] The positive electrode equipped with the positive-electrode binder layer which makes a subject a manganese content oxide and a nickel content oxide from the above result, A nonaqueous electrolyte rechargeable battery equipped with nonaqueous electrolyte equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium It turned out that it excels in an elevated-temperature preservation property by Li_2CO_3 containing in a positive-electrode binder layer by the content of this Li_2CO_3 being larger than 0 % of the weight, and being 5 or less % of the weight of the range, and excels in a load characteristic.
[0071]
[Effect of the Invention] The nonaqueous electrolyte rechargeable battery concerning this invention so that clearly from the above explanation At least one sort of 1st elements chosen from the group which consists of the metallic elements and boron (B) other than a lithium (Li), and manganese (Mn) and manganese, The manganese content oxide whose mole ratio [as opposed to the above-mentioned manganese including oxygen (O)] (the 1st element/manganese) of the 1st element of the above is within the limits of 0.5/1.5 or less [0.01/1.99 or more], At least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, and nickel (nickel) and nickel, The positive electrode equipped with the positive-electrode binder layer which makes a subject the nickel content oxide whose mole ratio (the 2nd element/nickel) of the 2nd element of the above to the above-mentioned nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] including oxygen, In a nonaqueous electrolyte rechargeable battery equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium, and nonaqueous electrolyte Li_2CO_3 contains in the above-mentioned positive-electrode binder layer, and into the positive-electrode binder layer, the content of this Li_2CO_3 is larger than 0 % of the weight, and let it be 5 or less % of the weight of the range. Therefore, according to this invention, the nonaqueous electrolyte cell which is excellent in an elevated-temperature preservation property and a load characteristic is realized.

[Translation done.]

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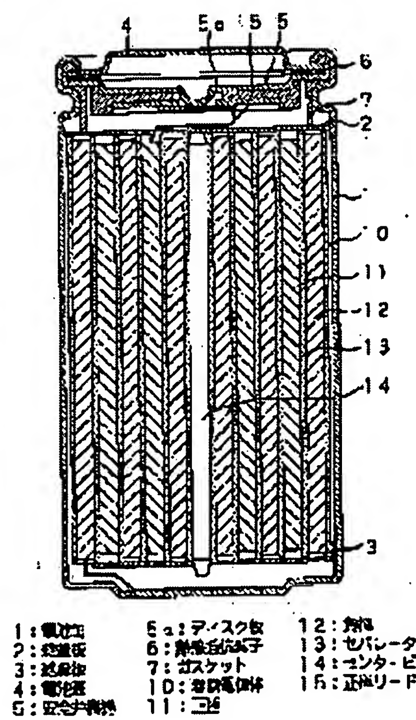
(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY



(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte secondary battery superior in high temperature storage characteristics and load characteristics.

SOLUTION: In the nonaqueous electrolyte secondary battery equipped with a positive electrode having a positive electrode mixture layer composed of manganese containing oxide and nickel containing oxide as the main body, with a negative electrode comprised by containing at least one kind among lithium metal, lithium alloy or a material capable of doping/de-doping lithium, and with the nonaqueous electrolyte, Li2CO3 is contained in the positive electrode mixture layer, and the content of the Li2CO3 is in the range larger than 0 wt.% and not more than 5 wt.% in the positive electrode mixture layer.

LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the nonaqueous electrolyte rechargeable battery equipped with the positive electrode containing the nickel content oxide containing the manganese content oxide, the lithium, and nickel (nickel) containing a lithium (Li) and manganese (Mn).
[0002]
[Description of the Prior Art] In recent years, with the advance of an electronic technique, many small portable electronic equipment, such as a camcorder/movie (video tape recorder), a cellular phone, or a laptop computer, spreads, and those miniaturizations and lightweight-izing are attained. Then, as a portable power source used for them, it is small and lightweight and development of the cell which has a high energy consistency, especially a rechargeable battery is furthered. The rechargeable lithium-ion battery which used nonaqueous electrolyte especially is greatly expected from high energy density being obtained compared with a lead cell or a nickel cadmium battery.
[0003] As a positive-electrode ingredient of this rechargeable lithium-ion battery, a lithium cobalt multiple oxide, a lithium manganese multiple oxide, lithium nickel complex oxide, etc. are put in practical use. Among these, the lithium cobalt multiple oxide is most excellent in the balance in each side, such as cell capacity, cost, and thermal stability, and is used widely now. On the other hand, although a lithium manganese multiple oxide has a fault, like cell capacity is low and some is bad as for an elevated-temperature preservation property and there is a fault, like thermal stability of lithium nickel complex oxide is low a little, these are excellent in the price of a raw material, and the field of adequate supply, and research is advanced towards the future activity. For example, while complementing both fault with recently by mixing and using a lithium manganese multiple oxide and lithium nickel complex oxide, the expansion and contraction of a positive electrode in charge and discharge are controlled, and the technique of raising a charge-and-discharge cycle property is proposed (refer to JP,8-45498,A).
[0004]
[Problem(s) to be Solved by the Invention] However, in the rechargeable battery currently indicated by JP,8-45498,A, when saved, for example under 45 degrees C - 60 degrees C hot environments, there was a problem that a property will fall. Although the capacity in a heavy load (condition that current density is large), and a high termination electrical potential difference was calculated when especially used for information terminals, such as a cellular phone, sufficient value was not able to be acquired after elevated-temperature preservation. Moreover, in the above-mentioned secondary ****, there was a problem that a charge-and-discharge cycle property could not fully be raised depending on the particle size of a lithium manganese multiple oxide and lithium nickel complex oxide.
[0005] Therefore, this invention is proposed for the purpose of offering the rechargeable battery which was excellent in the elevated-temperature preservation property, and was further excellent also in the load characteristic.
[0006]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention A

lithium (Li) and manganese (Mn), At least one sort of 1st elements chosen from the group which consists of the metallic elements and boron (B) other than manganese, The manganese content oxide whose mole ratio [as opposed to the above-mentioned manganese including oxygen (O)] (the 1st element/manganese) of the 1st element of the above is within the limits of 0.5/1.5 or less [0.01/1.99 or more], At least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, and nickel (nickel) and nickel, The positive electrode equipped with the positive-electrode binder layer which makes a subject the nickel content oxide whose mole ratio (the 2nd element/nickel) of the 2nd element of the above to the above-mentioned nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] including oxygen, In a nonaqueous electrolyte rechargeable battery equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium, and nonaqueous electrolyte Li2CO3 contains in the above-mentioned positive-electrode binder layer, and the content of this Li2CO3 is larger than 0 % of the weight in the above-mentioned positive-electrode binder layer, and is characterized by being 5 or less % of the weight of the range.
[0007] Since Li2CO3 contains the nonaqueous electrolyte rechargeable battery concerning this invention constituted as mentioned above in the positive-electrode binder layer with the content of the above-mentioned range, it is excellent in an elevated-temperature preservation property, and excellent in a load characteristic.
[0008]
[Embodiment of the Invention] Hereafter, the concrete example of this invention is explained in full detail with reference to a drawing.
[0009] The cross-section configuration of the nonaqueous electrolyte rechargeable battery concerning the gestalt of the 1 operation of this invention to drawing 1 is shown. This nonaqueous electrolyte rechargeable battery is called cylindrical [so-called], and has mostly the rolled electrode object 10 with which a band-like positive electrode 11 and a band-like negative electrode 12 were wound around the interior of the hollow cylinder-like cell can 1 through the separator 13. The cell can 1 is constituted by the iron (Fe) with which plating of nickel was carried out, the end section is closed, and the other end is opened wide. Inside the cell can 1, the electric insulating plates 2 and 3 of a pair are perpendicularly arranged to the winding peripheral surface, respectively so that the rolled electrode object 10 may be inserted.
[0010] the relief valve device 5 prepared in the open end section of the cell can 1 inside the cell lid 4 and this cell lid 4, and the feeling-of-heat resistance element (Positive Temperature Coefficient-TC component) 6 -- a gasket 7 -- minding -- by being closed, it is attached and the interior of the cell can 1 is sealed. The cell lid 4 is constituted by the same ingredient as the cell can 1. It connects with the cell lid 4 electrically through the feeling-of-heat resistance element 6, and disk plate 5a is reversed and the relief valve device 5 disconnects the electrical installation of the cell lid 4 and the rolled electrode object 10, when the internal pressure of a cell becomes more than fixed with an internal short circuit or heating from the outside. The feeling-of-heat resistance element 6 restricts a current according to increase of resistance, if temperature rises, it prevents unusual generation of heat by the high current, and is constituted by barium titanate system semiconductive ceramics. The gasket 7 is constituted by the insulating material and asphalt is applied to the front face.
[0011] The rolled electrode object 10 is wound focusing on the center pin 14. The positive-electrode lead 15 which consists of aluminum (aluminum) etc. is connected to the positive electrode 11 of the rolled electrode object 10, and the negative-electrode lead 16 which consists of nickel etc. is connected to the negative electrode 12. By welding the positive-electrode lead 15 to the relief valve device 5, it connects with the cell lid 4 electrically, and the negative-electrode lead 16 is welded to the cell can 1, and is connected electrically.
[0012] The positive electrode 11 is constituted by for example, the positive-electrode binder layer and the positive-electrode current collection body whorl, and has the structure where the positive-electrode binder layer was prepared in both sides or one side of a positive-electrode current collection body whorl. The positive-electrode current collection body whorl is constituted by metallic foils, such as aluminium

foil, a nickel foil, or a stainless steel foil.
[0013] In the positive-electrode binder layer, the manganese content oxide and nickel content oxide which are described below contain as positive active material, and binders, such as electric conduction material, such as a graphite, and polyvinylidene fluoride, contain further if needed.
[0014] And Li_2CO_3 contains in this positive-electrode binder layer. And the content of this Li_2CO_3 is larger than 0 % of the weight in the above-mentioned positive-electrode binder layer, and let it be 5 or less % of the weight of the range.
[0015] When Li_2CO_3 does not contain in a positive-electrode binder layer, an elevated-temperature preservation property is not improved. On the other hand, since there are many rates that Li_2CO_3 which does not contribute to electronic conduction occupies when the content of Li_2CO_3 in a positive-electrode binder layer exceeds 5 % of the weight, the conductivity of a positive electrode falls and a load characteristic falls.
[0016] Therefore, with a nonaqueous electrolyte rechargeable battery, it excels in an elevated-temperature preservation property by Li_2CO_3 containing in a positive-electrode binder layer by the content of this Li_2CO_3 being larger than 0 % of the weight to a positive-electrode binder layer, and being 5 or less % of the weight of the range, and excels in a load characteristic.
[0017] Manganese content oxide contains at least one sort of 1st elements chosen from the group which consists of the metallic elements and boron other than a lithium, manganese, and manganese, and oxygen. This manganese content oxide has for example, cubic (spinel) structure or tetragonal structure, and the 1st element is permuted by the manganese atom and exists in the site of a manganese atom part. When the chemical formula of a manganese content oxide expresses the 1st element with Ma, it is shown by $Li_xMn_{2-y}Ma_yO_4$. Here, the value of x is within the limits of $0.9<=x<=2$, and the value of y is within the limits of $0.01<=y<=0.5$. That is, presentation ratio Ma/Mn of the 1st element to manganese is or more 0.01/1.99 0.5/1.5 or less range in a mole ratio.
[0018] As the 1st element of the above, specifically Iron (Fe), cobalt (Co), Nickel (nickel), copper (Cu), zinc (Zn), aluminum (aluminum), Tin (Sn), chromium (Cr), vanadium (V), titanium (Ti), At least one sort chosen from the group which consists of magnesium (Mg), calcium (calcium), strontium (Sr), boron (B), a gallium (Ga), an indium (In), silicon (Si), and germanium (germanium) is desirable. The manganese content oxide which makes these the 1st element can be obtained comparatively easily, and is chemically stable.
[0019] Nickel content oxide contains at least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, nickel, and nickel, and oxygen. This nickel content oxide has the layer structure, and in a part of site of a nickel atom, the 2nd element is permuted by the nickel atom and exists. When the chemical formula of a nickel content oxide expresses the 2nd element with Mb, it is typically shown by $LiNi_{1-z}Mb_zO_2$. In addition, the presentation ratio of a lithium and oxygen may not be Li:O=1:2 and the value of z is within the limits of $0.01<=z<=0.5$. That is, presentation ratio Mb/nickel of the 2nd element to nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] in a mole ratio.
[0020] At least one sort chosen from the group which consists of iron, cobalt, manganese, copper, zinc, aluminum, tin, chromium, vanadium, titanium, magnesium, calcium, strontium, boron, a gallium, an indium, silicon, and germanium as the 2nd element of the above is desirable. It is because the nickel content oxide which makes these the 2nd element can be obtained comparatively easily and is chemically stable.
[0021] By permuting by other elements which mentioned above some of manganese or nickel, these manganese content oxide and a nickel content oxide can be considered that the crystal structure is stable, and, thereby, can raise an elevated-temperature preservation property now with this nonaqueous electrolyte rechargeable battery. It is because the heavy load discharge capacity after elevated-temperature preservation will fall if sufficient effectiveness cannot be acquired if making presentation ratio Ma/Mn of the 1st element to manganese or less [0.01/1.99 or more] into 0.5/1.5 by the mole ratio, and making presentation ratio Mb/nickel of the 2nd element to nickel or less [0.01/0.99 or more] into 0.5/0.5 by the mole ratio has few amounts of permutations than this, but there are more amounts of

permutations than this.
[0022] The mixing ratio of the manganese content oxide and nickel content oxide in a positive electrode 11 is a mass ratio, and it is desirable that they are the nickel content oxides 90-20 to the manganese content oxides 10-80. It is because a manganese content oxide deteriorates remarkably in the electrolyte later mentioned in an elevated-temperature ambient atmosphere, so internal resistance will increase after elevated-temperature preservation and capacity will fall, if there are more contents of a manganese content oxide than this. Moreover, a nickel content oxide is because discharge potential is low, so the heavy load discharge capacity in the high potential cut-off after elevated-temperature preservation will become low if there are more contents of a nickel content oxide than this.
[0023] As for the mean particle diameter of a manganese content oxide and a nickel content oxide, it is desirable that it is 30 micrometers or less, respectively. It is because the expansion and contraction of a positive electrode 11 accompanying charge and discharge cannot fully be controlled and sufficient charge-and-discharge cycle property cannot be acquired in ordinary temperature, if mean particle diameter is larger than this.
[0024] In addition, these manganese content oxide and nickel content oxide can be obtained by carrying out heating baking at the temperature of 600 degrees C - 1000 degrees C into an oxygen existence ambient atmosphere, after preparing the compound containing the compound containing a lithium compound, a manganese compound, and the 1st element or a lithium compound, a nickel compound, and the 2nd element, respectively and mixing by the ratio of a request of them. As a compound of a raw material, a carbonate, a hydroxide, an oxide, a nitrate, or an organic-acid salt is used, respectively in that case.
[0025] The negative electrode 12 has the structure where the negative-electrode binder layer was prepared in both sides or one side of a negative-electrode current collection body whorl, respectively, like the positive electrode 11. The negative-electrode current collection body whorl is constituted by metallic foils, such as copper foil, a nickel foil, or a stainless steel foil. The negative-electrode binder layer consists of potentials not more than 2V possible [occlusion and breaking away] including any one sort of the negative-electrode ingredient in which a dope and a dedope are possible, or two sorts or more in the lithium on the basis of for example, a lithium metal or lithium metal potential, for example, contains binders, such as polyvinylidene fluoride, further if needed.
[0026] A lithium metal and a lithium alloy compound are mentioned as a negative-electrode ingredient in which a dope and a dedope of a lithium are possible. A lithium alloy compound here is expressed for example, with the chemical formula DsEtLiu. In this chemical formula, D expresses at least one sort in the metallic element which can form a lithium, an alloy, or a compound, and a semi-conductor element, and E expresses at least one sort in metallic elements other than a lithium and D, and a semi-conductor element. Moreover, the values of s, t, and u are s> 0, t>=0, and u>=0, respectively.
[0027] Here, as the metallic element which can form a lithium, an alloy, or a compound, or a semi-conductor element, desirable especially preferably, 4B group's metallic element or semi-conductor element is silicon or tin, and is silicon most preferably. As the metal which can form a lithium, an alloy, or a compound, or a semi-conductor, each metals of Mg, B, aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, Bi, Cd, Ag, Zn, Hf, Zr, and Y, those alloy compounds, for example, Li-aluminum, Li-aluminum-M (M consists or more of one ofA [2],B [3], and 4B transition-metals elements among formula.) AlSb, CuMgSb, etc. can be mentioned. Moreover, these alloys or compounds are also desirable, for example, MxSi (M is one or more metallic elements except Si among a formula, and x is 0< x.) and MxSn (M is one or more metallic elements except Sn among a formula, and x is 0< x.) are mentioned. Specifically, SiB4, SiB6, Mg2Si, Mg2Sn, nickel2Si, TiSi2, MoSi2, CoSi2, NiSi2, CaSi2 and CrSi2, Cu5Si, FeSi2, MnSi2, NbSi2, TaSi2, VSi2 and WSi2, or ZnSi2 is mentioned.
[0028] Furthermore, as a negative-electrode ingredient, the lithium, the alloying or the element that can be compound-ized shown above, or a compound can also be used. That is, in this ingredient, one or more kinds of 4B group elements may be contained, and metallic elements other than 4B group containing a lithium may be contained. As such an ingredient, SiC, Si3N4, Si2N2O, germanium2N2O, SiOx (x are 0< x<=2 among a formula.), SnOx (x are 0< x<=2 among a formula.), LiSiO, LiSnO, etc.

can be illustrated.
[0029] As a negative-electrode ingredient in which a dope and a dedope of a lithium are possible, a carbon material, a metallic oxide, or polymeric materials is mentioned. As a carbon material, nongraphitizing carbon, an artificial graphite, corks, graphite, glassy carbon, an organic high molecular compound baking object, a carbon fiber, activated carbon, or carbon black is mentioned, for example. Among these, corks have pitch coke, needle coke, or petroleum coke, and an organic high-molecular-compound baking object says what calcinated and carbonized polymeric materials, such as phenol resin and furan resin, at suitable temperature to it. Moreover, as a metallic oxide, ferrous oxide, ruthenium oxide, molybdenum oxide, or the tin oxide is mentioned, and polyacethylene or polypyrrole is mentioned as polymeric materials.
[0030] The separator 13 is constituted by the porous membrane which consists of inorganic materials, such as a nonwoven fabric of the porous membrane which consists of an ingredient of polyolefine systems, such as polypropylene or polyethylene, or ceramics nature, and may be made into the structure which carried out the laminating of these two or more sorts of porous membrane..
[0031] The nonaqueous electrolyte which is liquefied nonaqueous electrolyte sinks into this separator 13. As for this nonaqueous electrolyte, lithium salt is dissolved in a non-aqueous solvent as an electrolyte salt. As a non-aqueous solvent, for example Propylene carbonate, ethylene carbonate, Diethyl carbonate, dimethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gamma-butyl lactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, 4-MECHIRU 1, 3-dioxolane, It is desirable, and diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propionitrile, an anisole, acetic ester, butylate, or propionic-acid ester mixes 1 of any sorts of these, and two sorts or more, and is used.
[0032] As lithium salt, there are LiClO4, LiAsF6, LiPF6, LiBF4, LiB (C6H5), LiCH3SO3, LiCF3SO3, LiCl, LiBr, etc., for example, and 1 of any sorts of these and two sorts or more are mixed, and are used.
[0033] The nonaqueous electrolyte rechargeable battery constituted as mentioned above is equipped with the positive-electrode binder layer which Li2CO3 contains, and it is larger than 0 % of the weight, and since content of Li2CO3 in a positive-electrode binder layer is made into 5 or less % of the weight of the range, it is excellent in an elevated-temperature preservation property and a load characteristic.
[0034] This nonaqueous electrolyte rechargeable battery can be manufactured as follows, for example.
[0035] first -- as positive active material -- a manganese content oxide and a nickel content oxide, and the need -- responding -- an electric conduction agent and a binder -- mixing -- a positive electrode -- a mixture is prepared. subsequently, this positive electrode -- a mixture -- solvents, such as a N-methyl-2-pyrrolidone, -- distributing -- a paste-like positive electrode -- a mixture -- it considers as a slurry. this positive electrode -- a mixture -- after applying a slurry to a positive-electrode current collection body whorl and drying a solvent, compression molding is carried out with a roller press machine etc., a positive-electrode binder layer is formed, and a positive electrode 11 is produced.
[0036] In this positive-electrode binder layer, Li2CO3 is larger than 0 % of the weight, and contains in 5 or less % of the weight of the range. the content of Li2CO3 in a positive-electrode binder layer -- a positive electrode -- it considers as the above-mentioned range by adjusting the addition of Li2CO3 suitably at the time of Shirabe of a mixture.
[0037] By the way, Li2CO3 may be used as one sort of the synthetic powder of a manganese content oxide. When using Li2CO3 as one sort of the synthetic powder of a manganese content oxide, Li2CO3 may remain in a manganese content oxide after composition. Thus, it is larger than 0 % of the weight in the content of Li2CO [in / using the positive active material with which Li2CO3 remains / a positive-electrode binder layer]3, and good also as 5 or less % of the weight.
[0038] In addition, what is necessary is to mix with what has the few amount of survival of Li2CO3 which remained in positive active material suitably, and just to let content of Li2CO3 finally contained in a positive-electrode binder layer be the above-mentioned range, when there are many amounts of survival of Li2CO3 which remained in positive active material after composition of a manganese content oxide since it was unreacted.
[0039] subsequently, a negative-electrode active material and the need -- responding -- a binder -- mixing -- a negative electrode -- a mixture -- preparing -- this negative electrode -- a mixture -- solvents,

such as a N-methyl-2-pyrrolidone, -- distributing -- a paste-like negative electrode -- a mixture -- it considers as a slurry. this negative electrode -- a mixture -- after applying a slurry to a negative-electrode current collection body whorl and drying a solvent, compression molding is carried out with a roller press machine etc., a negative-electrode binder layer is formed, and a negative electrode 12 is produced.
[0040] Then, while attaching the positive-electrode lead 15 in a positive-electrode current collection body whorl by welding etc., the negative-electrode lead 16 is attached in a negative-electrode current collection body whorl by welding etc. Then, on both sides of the positive electrode 11 and negative electrode 12 which welded the point of the negative-electrode lead 16 to the cell can 1, and wound the positive electrode 11 and the negative electrode 12 while welding the point of winding and the positive-electrode lead 15 to the relief valve device 5 through the separator 13, it contains inside the cell can 1 with the electric insulating plates 2 and 3 of a pair. After containing a positive electrode 11 and a negative electrode 12 inside the cell can 1, nonaqueous electrolyte is poured into the interior of the cell can 1, and a separator 13 is infiltrated.
[0041] then, the open end of the cell can 1 -- the cell lid 4, the relief valve device 5, and the feeling-of-heat resistance element 6 -- a gasket 7 -- minding -- it fixes by closing. Thereby, the nonaqueous electrolyte rechargeable battery shown in drawing 1 is formed.
[0042] In addition, this invention can be suitably changed in the range which is not limited to an above-mentioned publication and does not deviate from the summary of this invention.
[0043] Therefore, in the above, although an example was given concretely and explained about the cylindrical nonaqueous electrolyte rechargeable battery which has winding structure, this invention is applicable also about the cylindrical nonaqueous electrolyte rechargeable battery which has other configurations. Moreover, it is applicable similarly about the nonaqueous electrolyte rechargeable battery which has various configurations, such as a mold with which it is not limited to a cylindrical shape about the configuration of a cell, and the electrode component was enclosed with the interior of coin molds other than cylindrical, a carbon button mold, a square shape, or a laminate film.
[0044] Moreover, although the case where the nonaqueous electrolyte which comes to dissolve an electrolyte salt in a non-aqueous solvent as nonaqueous electrolyte was used in the above was mentioned as the example and explained The gel electrolyte which this invention is not limited to this and consists of an electrolyte salt, a swelling solvent, and a matrix macromolecule as nonaqueous electrolyte, It can apply, also when the nonaqueous electrolyte ingredient which comes to mix the inorganic solid electrolyte which uses as a principal component the solid polymer electrolyte which makes-izing [an ion conductivity macromolecule and an electrolyte salt] come [compound], the ion conductivity inorganic ceramics, glass, an ionicity crystal, etc., and nonaqueous electrolyte is used.
[0045] For example, when using a gel electrolyte as nonaqueous electrolyte, as long as the ionic conductivity of a gel electrolyte is 1 or more mS/cm, the structure of the matrix macromolecule which constitutes the presentation of a gel electrolyte and a gel electrolyte may be what kind of thing.
[0046] As a concrete matrix giant molecule, it is possible to use the copolymer of a polyacrylonitrile, polyvinylidene fluoride, polyvinylidene fluoride, and poly hexafluoropropylene, polytetrafluoroethylene, poly hexafluoropropylene, polyethylene oxide, polypropylene oxide, poly FOSUFAZEN, a polysiloxane, polyvinyl acetate, polyvinyl alcohol, a polymethyl methacrylate, polyacrylic acid, polymethacrylic acid, a styrene butadiene rubber, nitril-butadiene rubber, polystyrene, a polycarbonate, etc. When electrochemical stability is especially taken into consideration, it is desirable to use a polyacrylonitrile, polyvinylidene fluoride, poly hexafluoropropylene, polyethylene oxide, etc.
[0047] Moreover, although it is difficult to specify generally from changing with compatibility of a matrix macromolecule and nonaqueous electrolyte, as for the weight of a matrix macromolecule required in order to produce a gel electrolyte, it is desirable to consider as 5 % of the weight - 50 % of the weight to nonaqueous electrolyte.
[0048]
[Example] Hereafter, this invention is explained based on a concrete experimental result.
[0049] an example 1 [production of a positive electrode] -- the manganese content oxide which mixes a lithium carbonate (Li_2CO_3), a manganese dioxide (MnO_2), and 3 oxidation Nichrome (CrO_3),

calcinates at the temperature of 850 degrees C for 5 hours, and contains chromium as a lithium, manganese, and the 1st element (Ma) in air first was produced.
[0050] Moreover, a lithium hydroxide (LiOH), 1 nickel oxide (NiO), and 1 cobalt oxide (CoO) were mixed, and the nickel content oxide which calcinates at the temperature of 750 degrees C for 5 hours, and contains cobalt as a lithium, nickel, and the 2nd element (Mb) in air was produced.
[0051] Subsequently, positive active material was obtained by mixing them as 50:50 by the weight ratio, after grinding the manganese content oxide and nickel content oxide which were obtained, respectively.
[0052] Moreover, the content of Li2CO3 contained in positive active material was 0.01 % of the weight. In addition, as measurement of the content of Li2CO3 contained in positive active material was shown below, it was performed.
[0053] First, the sulfuric acid decomposed the positive-active-material sample, and CO2 was made to generate. Subsequently, the solution of barium chloride and a sodium hydroxide was made to absorb this CO2. Subsequently, this solution was titrated with the acid standard solution, and the quantum of CO2 was carried out. And it converted from this CO2 amount and asked for the content of Li2CO2 contained in positive active material.
[0054] subsequently, this positive-active-material 91 weight section -- receiving -- as an electric conduction agent -- as the GURAFAITO 6 weight section and a binder -- the Pori fluoride PINIRIDEN 3 weight section -- mixing -- a positive electrode -- the mixture was prepared. and this positive electrode -- the mixture was dried and the positive electrode of a pellet type was obtained by the thing whose diameter is 15.5mm and which is fabricated disc-like.
[0055] [Production of a negative electrode] After applying the coal tar system pitch as a binder to the coal system corks 100 weight section as a filler for 30 weight sections and mixing at about 100 degrees C first, compression molding was carried out with the press machine, and the carbon molding object was produced by heat-treating at the temperature of 1000 degrees C or less. Then, after repeating pitch sinking in / heat treatment process which sinks in and heat-treats the coal tar system pitch which carried out melting to this carbon molding object below 200 degrees C below 1000 degrees C several times, in **************, it heat-treated at 2700 degrees C, and the graphitization molding object was produced. Then, grinding classification of this graphitization molding object was carried out, and it was presupposed that it is powdered.
[0056] When structural analysis was performed with the X-ray diffraction method about the obtained graphitization powder, the spacing of a field (002) was 0.337nm and C shaft microcrystal thickness of a field (002) was 50.0nm. Moreover, the true density for which it asked by the pycnometer was 2.23 g/cm3, bulk density was 0.83 g/cm3, and the average shape parameter was 10. furthermore, BET (Brunauer, Emmett, Teller) -- the specific surface area for which it asked by law was 4.4m2/g, and, for 31.2 micrometers and 10% particle size of accumulation, 12.3 micrometers and 50% particle size of accumulation were [mean particle diameter / 29.5 micrometers and a total of 90% particle size of the particle size distribution searched for with the laser diffraction method] 53.7 micrometers. In addition, the disruptive strength of the graphitization particle for which it asked using the Shimazu very small compression tester (Shimadzu make) was 7.0x107Pa by the average.
[0057] subsequently, the above-mentioned graphitization powder 35 weight section and the Mg2Si powder 55 weight section which are a negative-electrode active material -- as a binder -- the polyvinylidene fluoride 10 weight section -- mixing -- a negative electrode -- N-methyl pyrrolidone which a mixture is prepared and is a solvent -- distributing -- a negative electrode -- a mixture -- it considered as the slurry. and this negative electrode -- a mixture -- apply a slurry to homogeneity and both sides of the negative-electrode current collection body whorl which consists of band-like copper foil with a thickness of 10 micrometers were made to dry it, compression molding was carried out with the roll press machine, the negative-electrode binder layer was formed, and the negative electrode was produced by piercing to discoid with a diameter of 16mm.
[0058] [Preparation of nonaqueous electrolyte] The nonaqueous electrolyte which makes it come as an electrolyte salt into the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity % to dissolve LiPF6 at a rate of 1.0 mols/l. was prepared.

[0059] Using the positive electrode, the negative electrode, and nonaqueous electrolyte which were produced as mentioned above, below, as the nonaqueous electrolyte rechargeable battery of a coin mold was shown below, it was produced.
[0060] First, after containing the negative electrode with the negative-electrode can which consists of stainless steel and pouring nonaqueous electrolyte into a negative-electrode can, the separator which is the thickness of 50 micrometers in the product made from fine porosity polypropylene was allotted on the negative electrode. Subsequently, after arranging the positive electrode and pouring in nonaqueous electrolyte on a separator, the nonaqueous electrolyte rechargeable battery of a coin mold with an outer diameter [of 20mm] and a height of 1.6mm was obtained for the positive-electrode can equipped with the three-tiered structure which consists of aluminum, stainless steel, and nickel a negative-electrode can and by fixing in total through the obturation gasket made from polypropylene.
[0061] The content of Li2CO3 in examples 2 and 3 and the example 1 of a comparison - 3 positive-electrode binder layer produced the nonaqueous electrolyte rechargeable battery like the example 1 except being as in Table 1 shown below. In addition, the content of Li2CO3 was controlled by carrying out adding after mixing of Li2CO3.
[0062] After performing constant current constant-potential charge until cell voltage amounted to 4.2V in 1mA constant current first to the nonaqueous electrolyte rechargeable battery of the examples 1-3 produced as mentioned above and the examples 1-3 of a comparison, the charge-and-discharge cycle which carries out constant-current discharge to termination electrical-potential-difference (cut-off voltage) 2.5V by 1mA constant current was performed, and initial discharge capacity was measured.
[0063] Subsequently, in order to evaluate an elevated-temperature preservation property and a load characteristic, the charge and discharge test shown below was performed.
[0064] The charge-and-discharge cycle mentioned above was again performed after measurement of an initial <evaluation of elevated-temperature preservation property> above-mentioned discharge capacity. Subsequently, it saved for two weeks in 60-degree-C oven. Subsequently, once discharging to termination electrical-potential-difference 2.5V under 23-degree-C environment, discharge capacity was measured for the charge-and-discharge cycle as it is **** 10 cycles. And the peak price was made into recovery capacity among the acquired discharge capacity value, and it asked for the ratio of recovery capacity to initial discharge capacity by the percentage, and considered as the recovery capacity maintenance factor.
[0065] After charging until cell voltage amounted to 4.2V in <evaluation of load characteristic> 1mA constant current, the discharge capacity in 0.1C was measured and the discharge capacity in 3C was measured further. And it asked for the capacity factor (%) of 3C discharge capacity to 0.1C discharge capacity, and this capacity factor estimated the load characteristic.
[0066] The above measurement result is shown in Table 1 in accordance with the content of Li2CO3 in a positive-electrode binder layer.
[0067]
[Table 1]

	Li_2CO_3	初期	高温保存特性		負荷特性
	(重量%)	放電容量 (mAh)	回復容量維持率(%)	回復容量 (mAh)	容量比 (%)
実施例1	0.01	8.53	85.1	7.26	8.01
実施例2	2.0	8.37	88.7	7.42	78.2
実施例3	5.0	8.11	89.1	7.23	76.4
比較例1	0	8.54	76.3	6.51	80.2
比較例2	5.5	8.07	89.2	7.20	73.1
比較例3	10.0	7.69	89.4	6.87	31.4

Table 1 shows that the nonaqueous electrolyte rechargeable battery of an example 1 - an example 3 is excellent in an elevated-temperature preservation property and a load characteristic. Moreover, it turns out that an elevated-temperature preservation property improves, so that the content of Li2CO3 in a positive-electrode binder layer is made to increase.

[0068] However, since Li_2CO_3 which does not contribute to electronic conduction contains superfluously in a positive-electrode binder layer in the case of the nonaqueous electrolyte rechargeable battery of the example 2 of a comparison for which the content of Li_2CO_3 exceeds 5 % of the weight, and the example 3 of a comparison, it turns out that the conductivity of a positive electrode falls and a load characteristic falls.
[0069] Moreover, since the nonaqueous electrolyte rechargeable battery of the example 1 of a comparison whose content of Li_2CO_3 is 0 % of the weight has the bad elevated-temperature preservation property, it turns out that it is not desirable practically.
[0070] The positive electrode equipped with the positive-electrode binder layer which makes a subject a manganese content oxide and a nickel content oxide from the above result, A nonaqueous electrolyte rechargeable battery equipped with nonaqueous electrolyte equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium It turned out that it excels in an elevated-temperature preservation property by Li_2CO_3 containing in a positive-electrode binder layer by the content of this Li_2CO_3 being larger than 0 % of the weight, and being 5 or less % of the weight of the range, and excels in a load characteristic.
[0071]
[Effect of the Invention] The nonaqueous electrolyte rechargeable battery concerning this invention so that clearly from the above explanation At least one sort of 1st elements chosen from the group which consists of the metallic elements and boron (B) other than a lithium (Li), and manganese (Mn) and manganese, The manganese content oxide whose mole ratio [as opposed to the above-mentioned manganese including oxygen (O)] (the 1st element/manganese) of the 1st element of the above is within the limits of 0.5/1.5 or less [0.01/1.99 or more], At least one sort of 2nd elements chosen from the group which consists of the metallic elements and boron other than a lithium, and nickel (nickel) and nickel, The positive electrode equipped with the positive-electrode binder layer which makes a subject the nickel content oxide whose mole ratio (the 2nd element/nickel) of the 2nd element of the above to the above-mentioned nickel is within the limits of 0.5/0.5 or less [0.01/0.99 or more] including oxygen, In a nonaqueous electrolyte rechargeable battery equipped with the negative electrode with which at least one or more kinds in the ingredient in which a dope and a dedope are possible come to contain a lithium metal, a lithium alloy, or a lithium, and nonaqueous electrolyte Li_2CO_3 contains in the above-mentioned positive-electrode binder layer, and into the positive-electrode binder layer, the content of this Li_2CO_3 is larger than 0 % of the weight, and let it be 5 or less % of the weight of the range. Therefore, according to this invention, the nonaqueous electrolyte cell which is excellent in an elevated-temperature preservation property and a load characteristic is realized.

[Translation done.]